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(54) [Title of the Invention]

METHOD FOR MANUFACTURING SOFT MAGNETIC ALLOY PLATED THIN
FILM, SOFT MAGNETIC ALLOY PLATED THIN FILM, AND THIN FILM
MAGNETIC HEAD

(57) [Abstract]

[Object]

To obtain a soft magnetic alloy plated thin film having
high saturation magnetic flux density, excellent in soft
magnetic characteristics, having high specific resistance,
and excellent in writing and reading characteristics.

[Means for Solving]

Form a soft magnetic alloy plated thin film by supplying divalent ions of Co, Ni and Fe to a plating solution by a salt containing the divalent ions of Co, Ni and Fe, adding at least one kind of molybdate ions, tungstate ions, vanadate ions, and chromium(III) ions to the plating solution, and performing electroplating in the plating solution of ion concentration of added ions of from 1×10^{-5} to 2×10^{-4} mol/l.

[Claims]

[Claim 1] A method for manufacturing a soft magnetic alloy plated thin film comprising supplying divalent ions of Co, Ni and Fe to a plating solution by a salt containing the divalent ions of Co, Ni and Fe, adding at least one kind of molybdate ions, tungstate ions, vanadate ions, and chromium(III) ions to the plating solution, and performing electroplating in the plating solution of ion concentration of added ions of from 1×10^{-5} to 2×10^{-4} mol/l to thereby form a soft magnetic alloy plated thin film.

[Claim 2] The method for manufacturing a soft magnetic alloy plated thin film as claimed in claim 1, wherein the salt for supplying the divalent ions of Co, Ni and Fe to the plating solution is sulfate and/or hydrochloride.

[Claim 3] The method for manufacturing a soft magnetic alloy plated thin film as claimed in claim 1 or 2, wherein the added ions are two or more kinds.

[Claim 4] The method for manufacturing a soft magnetic alloy plated thin film as claimed in claim 1, 2 or 3, wherein the Co ion concentration in the plating solution is from 0.05 to 0.1 mol/l, the Ni ion concentration is from 0.2 to 0.3 mol/l, and the Fe ion concentration is from 0.01 to 0.3 mol/l.

[Claim 5] The method for manufacturing a soft magnetic alloy plated thin film as claimed in claim 4, wherein the electric current density at the time of electroplating is 6.0 mA/cm² or less.

[Claim 6] The method for manufacturing a soft magnetic alloy plated thin film as claimed in claim 4 or 5, wherein the pH of the plating solution is from 2 to 4.

[Claim 7] The method for manufacturing a soft magnetic alloy plated thin film as claimed in claim 4, 5 or 6, wherein a magnetic field of 50 gauss or more is applied at the time of electroplating.

[Claim 8] A method for manufacturing a soft magnetic alloy plated thin film having high saturation magnetic flux density and high specific resistance, which comprises supplying divalent ions of Co, Ni and Fe to a plating solution by sulfate and/or hydrochloride containing the divalent ions of Co, Ni and Fe, adding at least two kinds of molybdate ions, tungstate ions, vanadate ions, and chromium(III) ions to the plating solution, adjusting the added ion concentration to from 1×10^{-5} to 2×10^{-4} mol/l, and the Co ion concentration to from

0.05 to 0.1 mol/l, the Ni ion concentration to from 0.2 to 0.3 mol/l, and the Fe ion concentration to from 0.01 to 0.3 mol/l, and the pH of the plating solution to from 2 to 4, and performing electroplating in the plating solution with applying a prescribed intensity of a magnetic field.

[Claim 9] A soft magnetic alloy plated thin film manufactured by the method for manufacturing a soft magnetic alloy plated thin film as claimed in any of claims 1 to 8, which comprises Co, Ni and Fe as the main components, and contains any one kind or more of Mo, W, V and Cr in an amount of from 1 to 5 at% as addition element(s).

[Claim 10] The soft magnetic alloy plated thin film as claimed in claim 9, wherein the Co content in the plated film is from 50 to 90 at%, and the Fe content is from 5 to 10 at%.

[Claim 11] The soft magnetic alloy plated thin film as claimed in claim 9 or 10, wherein the specific resistance of the plated film is $30 \mu\Omega \cdot \text{cm}$ or more, the saturation magnetic flux density is 1.5T or more, and the magnetostriction constant is 3×10^{-6} or less.

[Claim 12] A thin film magnetic head having an inductive head performing magnetic recording on a magnetic recording medium by generating a magnetic field between the tips of upper and lower magnetic pole layers formed up and down via a recording gap layer by lamination, wherein one or both of the upper and lower magnetic pole layers are constituted of the

soft magnetic alloy plated thin film as claimed in claim 9, 10 or 11.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a plated thin film mainly used as the magnetic pole of a thin film magnetic head suitable for high density magnetic recording, which is a soft magnetic alloy plated thin film high in saturation magnetic flux density, specific resistance and coercive force, and low in magnetostriction constant, the manufacturing method of the same, and also relates to a thin film magnetic head in which the soft magnetic alloy plated thin film is used as the magnetic pole layer of an inductive head.

[0002]

[Prior Art]

In recent years, plated thin films are widely used not only for ornamentation and corrosion resistance but also in electronic parts as functional thin films. For example, in the thin film magnetic head of hard disc drive that is external storage for computer, a permalloy alloy thin film manufactured by a plating method is used as the magnetic substance constituting the magnetic pole layer of an inductive head.

[0003]

Permalloy is a typical soft magnetic alloy material for

use in plated thin films, and especially a permalloy alloy comprising Ni_{82} at% and Fe_{18} at% is characterized in that it has a zero or negative magnetostriction constant.

[0004]

The increase of capacity and miniaturization are strongly required of the hard disc drive year by year. The increase in density has been advanced with the trend, and materials having high saturation magnetic flux density have been demanded as the magnetic substance of head.

[0005]

However, when Fe content is increased for obtaining high saturation magnetic flux density with a permalloy film, a magnetostriction constant rises, so that the structure of magnetic domain becomes unstable. Accordingly, there is restriction in heightening of saturation magnetic flux density with a permalloy film to be used as the magnetic pole layer of a thin film magnetic head.

[0006]

Fig. 1 is a drawing showing the distribution of saturation magnetic flux densities in a Co-Ni-Fe ternary series alloy. The area shown by A in the Figure is high in saturation magnetic flux density and small in magnetostriction constant, so that it is supposed to be promising as the magnetic materials of a thin film magnetic head. A Co-Ni-Fe ternary series alloy plated thin film having a magnetostriction constant of 0 and

high saturation magnetic flux density is disclosed in U.S. Patent 4,661,216.

[0007]

However, in the compositional region of the above-described conventional Co-Ni-Fe ternary series alloy plated thin film, the value of effective specific resistance is as low as $10 \mu\Omega \cdot \text{cm}$, so that writing characteristics in a high frequency region are unstable.

[0008]

For the purpose of the improvement of writing characteristics in the high frequency region, increasing of specific resistance of plated thin films has been tried. Heightening of specific resistance by the addition of Mo to $\text{Ni}_{80}\text{Fe}_{20}$ of conventional material is discussed in the collection of outlines in the scientific lecture meeting of Society of Japan Applied Magnetism, p. 207 (1998). According to the literature, a soft magnetic plated thin film having zero magnetostriction and about $47 \mu\Omega \cdot \text{cm}$ can be obtained in an $\text{Mo}_3\text{Ni}_{80}\text{Fe}_{17}$ film added with about 3 at% of Mo. However, there is such a problem that the saturation magnetic flux density is as low as about 1.0T.

[0009]

Further, for the purpose of obtaining high saturation magnetic flux density, a plated film having high specific resistance utilizing $\text{Ni}_{45}\text{Fe}_{55}$ having high saturation magnetic

flux density as compared with $\text{Ni}_{80}\text{Fe}_{20}$ is also discussed. Saturation magnetic flux density of from 1.5 to 1.6T and specific resistance of from 50 to 60 $\mu\Omega\cdot\text{cm}$ have been realized by introducing from 1 to 3 at% of addition element into $\text{Ni}_{45}\text{Fe}_{55}$ as disclosed in JP-A-9-63016 (the term "JP-A" as used herein refers to an "unexamined published Japanese patent application"). However, the soft magnetic plated thin film is problematic in the point that magnetostriction is as high as $+5\times 10^{-6}$ or so.

[0010]

As described above, a soft magnetic alloy thin film having high specific resistance, high saturation magnetic flux density and zero magnetostriction according to a plating method excellent in productivity, and a manufacturing method of the same have not been developed yet.

[0011]

[Problems that the Invention is to Solve]

An object of the invention is to provide a magnetic alloy thin film mainly used as the magnetic substance of a thin film magnetic head suitable for high density magnetic recording manufactured by a plating method, which is a plated thin film having high saturation magnetic flux density, excellent in soft magnetic characteristics, having high specific resistance, and excellent in writing and reading characteristics, and another object is to provide a manufacturing method of the same.

[0012]

[Means for Solving the Problems]

As described above, although saturation magnetic flux density is high, specific resistance is small with Co-Ni-Fe ternary alloy plated thin film. Therefore, for obtaining a plated thin film having high saturation magnetic flux density and high specific resistance, the present inventors have examined to introduce Mo, Cr, W and V to a plated film by the addition of additives to a plating bath at the time of Co-Ni-Fe ternary alloy plating, and made various experiments, thus the present invention has been accomplished.

[0013]

That is, a method for manufacturing a soft magnetic alloy plated thin film of the invention comprises supplying divalent ions of Co, Ni and Fe to a plating solution by a salt containing the divalent ions of Co, Ni and Fe, adding at least one kind of molybdate ions, tungstate ions, vanadate ions, and chromium(III) ions to the plating solution, and performing electroplating in the plating solution of ion concentration of added ions of from 1×10^{-5} to 2×10^{-4} mol/l to thereby form a soft magnetic alloy plated thin film. According to such a manufacturing method, a soft magnetic alloy plated thin film comprising Co, Ni and Fe as the main components and from 1 to 5 at% of any one or more kinds of Mo, W, V and Cr as the addition elements is formed.

[0014]

As the characteristics indispensable to magnetic substances of a thin film magnetic head capable of coping with high density recording, high frequency responsibility is exemplified. As the frequency of magnetization response of a thin film magnetic head increases, that is, as the magnetization fluctuation of the magnetic substance of a thin film magnetic head per unit time increases, over-current passing through the magnetic substance increases. The over-current generates magnetic flux that hinders magnetic flux fluctuation according to Lenz's law. As a result, magnetization fluctuation is restrained as signals approach high frequency. Here, the over-current passing through the magnetic substance is inversely proportional to the specific resistance of the magnetic substance. Accordingly, to obtain good high frequency characteristics, a magnetic substance is required to be high specific resistance.

[0015]

Therefore, when the specific resistance of the magnetic substance is increased by admixing impurities in a plated film, the reduction of magnetization fluctuation due to over-current is restrained, so that high frequency responsibility is improved. In the invention, the reason to introduce Mo, Cr, W and V into a Co-Ni-Fe ternary alloy plated film is to utilize the increase in specific resistance.

[0016]

Further, since magnetic media using magnetic substances having high coercive force are used according to the increased recording density of hard disc apparatus in recent years, magnetic substances constituting the magnetic pole layer of a thin film magnetic head are required to have high saturation magnetic flux density. From the experiments by the present inventors, it has been clarified that if the composition ratio of the addition elements is too large, saturation magnetic flux density becomes small and characteristics as the magnetic substance of a magnetic head for high density hard discs cannot be obtained. That the concentration of ions to be added is restricted to a specific range in the invention is for this reason.

[0017]

In a thin film magnetic head having an inductive head for performing magnetic recording on a magnetic recording medium by generating a magnetic field between the tips of upper and lower magnetic pole layers formed up and down via a recording gap layer by lamination, when one or both of the upper and lower magnetic pole layers are formed by the manufacturing method of a soft magnetic alloy plated thin film, the magnetic pole layers have high specific resistance, so that excellent in high frequency characteristics and at the same time high in saturation magnetic flux density and low in magnetostriction,

so that the thin film magnetic head has very good reproducing and recording characteristics and capable of withstanding further high speed and high density magnetic recording.

[0018]

[Mode for Carrying Out the Invention]

The preferred embodiments of the invention are described below. A plating solution for use in the manufacturing method of the invention can supply divalent ions of Fe, Co and Ni by sulfate and/or hydrochloride. Further, the plating solution contains any one kind or more, preferably two kinds or more, of molybdate ions, tungstate ions, vanadate ions, and chromium(III) ions. The contents of Co, Ni and Fe in the plating solution are adjusted according to plating conditions.

[0019]

For obtaining a film having a smaller magnetostriction constant, the composition ratio of Fe in the film is preferably smaller (that is, the Fe ion concentration in a plating solution is preferably lower). The concentrations of Co, Fe and Ni ions in a plating solution are respectively preferably Co^{2+} of from 0.05 to 0.1 mol/l, Ni^{2+} of from 0.2 to 0.3 mol/l, and Fe^{2+} of from 0.01 to 0.3 mol/l.

[0020]

For obtaining higher specific resistance, the composition ratio (at%) of Mo, Cr, W and V in a plated film is preferably higher. For obtaining higher saturation

magnetic flux density, the composition ratio (at%) of Mo, Cr, W and V is preferably lower. From these factors, the preferred composition ratio of Mo, Cr, W and V in a plated film is from 1 to 5 at%.

[0021]

The concentrations of molybdate ions, tungstate ions, vanadate ions, and chromium (III) ions in a plating solution are adjusted according to plating conditions. For obtaining higher specific resistance, the concentrations of molybdate ions, tungstate ions, vanadate ions, and chromium (III) ions in a plating solution are preferably higher. For obtaining higher saturation magnetic flux density, the concentrations of molybdate ions, tungstate ions, vanadate ions, and chromium (III) ions in a plating solution are preferably lower. Accordingly, for obtaining a soft magnetic alloy plated thin film having high saturation magnetic flux density and high specific resistance, the total addition ion concentration of molybdate ions, tungstate ions, vanadate ions, and chromium(III) ions in a plating solution is preferably the range of from 1×10^{-5} to 2×10^{-4} mol/l.

[0022]

For stably obtaining a plated film, a stress relaxing agent, a surfactant and a pH buffer are generally used, and the concentrations are arbitrarily adjusted. For stably obtaining a smooth plated film, the pH of the plating solution

is preferably from 2 to 4. When the pH exceeds 4, Fe^{2+} is oxidized. While when the pH is less than 2, hydrogen is generated on the surface of a substance to be plated, as a result the control of the thickness of a plating film becomes difficult and the surface of the plated film to be obtained is coarse.

[0023]

For obtaining higher saturation magnetic flux density, it is preferred that the content of Co in the plated magnetic substance is 50% or more, and Fe content is 5% or more. For obtaining excellent soft magnetic characteristics, it is preferred that the Co content is 90% or less, and Fe content is 20% or less. For making magnetostriction constant approach the value of 0, the content of Fe in the film is preferably 10% or less.

[0024]

For obtaining excellent soft magnetic characteristics, it is preferred that a magnetic field, preferably a magnetic field of 50 gauss or higher, is applied at the time of plating. For obtaining a smooth surface, current density at the time of plating is preferably 6.0 mA/cm^2 or less.

[0025]

Example

A manufacturing test of a soft magnetic alloy plated thin film according to the invention was performed with a paddle stirring type plating bath having the form as shown in Fig.

2. The plating bath comprises plating tank 1 made of acrylic resin and plating solution 5 is supplied thereto.

[0026]

In plating layer 1, cathode 2 installing a wafer that is a material to be plated is arranged at the lower part and anode 3 is arranged at the upper part. Paddle 4 reciprocates in plating tank 1. A magnetic field is applied in the perpendicular direction to the paddle movement, and the intensity of the magnetic field is 500 gauss. The temperature, pH and concentration of plating solution 5 are controlled in plating layer 1 and in the channel. Plating solution 5 is supplied with a pump, and an overflowed solution is recovered and returned to the plating tank. The quantity of flow is adjusted with a flow adjusting valve.

[0027]

As the wafer, a glass substrate or a sintered body of alumina and titanium carbide was used, and a permalloy alloy film (thickness: 1,000 Å) was formed as the under film by sputtering in use.

[0028]

Plating solution 5 contains 0.04 mol/l of cobalt sulfate heptahydrate, 0.04 mol/l of cobalt chloride hexahydrate, 0.115 mol/l of nickel sulfate hexahydrate, 0.115 mol/l of nickel chloride hexahydrate, and 0.01 mol/l of iron sulfate heptahydrate. In addition, 10 mol/l of boric acid as the pH

buffer, 1.5 g/l of sodium saccharin for the stress reduction of a plating thin film, and 0.1 g/l of sodium dodecylbenzenesulfonate as the surfactant of a plating thin film were added. Further, as the addition elements, sodium molybdate, sodium tungstate, ammonium vanadate, and chromium(III) sulfate were added. Further, the pH of the plating solution was adjusted to 3.0 with hydrochloric acid. The temperature of the plating solution was set at $35 \pm 0.1^\circ\text{C}$ with an electron thermostatic apparatus. The feeding amount of the plating solution to the plating tank was 4 liters per every minute.

[0029]

Figs. 3 and 4 show the composition of the plated film, the specific resistance, and the saturation magnetic flux density to the concentration of molybdate ions in the plating solution, respectively. By the addition of molybdate ions to the plating solution, Mo at% in the plated film increased, and conspicuous effect was observed in the increase in specific resistance. By the addition of molybdate ions to the plating solution, the saturation magnetic flux density monotonously reduced. The similar effect of the increase in specific resistance was observed when tungstate ions, vanadate ions, and chromium(III) ions were added.

[0030]

Further, the relationships between the film composition and the magnetostriction constant, and the saturation magnetic

flux density in the plated films of various compositions obtained by changing Co^{2+} , Fe^{2+} and Ni^{2+} concentrations in the plating bath are shown in Table 1 below. Incidentally, in Table 1, the data that showed unsuitable characteristics to be used as the magnetic pole layer of the thin film magnetic head corresponding to high recording density were underlined.

[0031]

Table 1

	Composition of Film (at%)	Specific Resistance ($\mu\Omega \cdot \text{cm}$)	Saturation Magnetic Flux Density (T)	Magnetostriiction Constant (10^{-6})
Comparative Example 1	$\text{Fe}_{17}\text{Ni}_{80}\text{Mo}_3$	47	<u>1.0</u>	-0.3
Comparative Example 2	$\text{Fe}_{57}\text{Ni}_{42}\text{Mo}_1$	60	1.5	<u>4.2</u>
Comparative Example 3	$\text{Fe}_{23}\text{Co}_{65}\text{Ni}_{12}$	<u>21</u>	2.0	2.0-7.0
Example 1	$\text{Fe}_{10}\text{Co}_{58}\text{Ni}_{29}\text{Mo}_3$	41	1.5	2.8
Example 2	$\text{Fe}_6\text{Co}_{79}\text{Ni}_{13}\text{Mo}_2$	32	1.7	1.5
Comparative Example 4	$\text{Fe}_3\text{Co}_{68}\text{Ni}_{27}\text{Mo}_2$	<u>25</u>	<u>1.2</u>	0.8
Comparative Example 5	$\text{Fe}_{13}\text{Co}_{69}\text{Ni}_{15}\text{Mo}_3$	44	1.6	<u>4.9</u>
Comparative Example 6	$\text{Fe}_8\text{Co}_{45}\text{Ni}_{44}\text{Mo}_3$	31	<u>1.1</u>	1.1
Comparative Example 7	$\text{Fe}_6\text{Co}_{91}\text{Ni}_2\text{Mo}_1$	<u>27</u>	<u>1.2</u>	1.5

[0032]

As is apparent from the results shown in Table 1, the magnetostriction constant increases with the increase of Fe composition in the film. In addition, a soft magnetic plated thin film having both saturation magnetic flux density of 1.5T or more and low magnetostriction of 3×10^{-6} or less was obtained by Fe composition ratio in the film of from 5 to 10 at%.

[0033]

[Advantage of the Invention]

The plated thin film of the invention is high in saturation magnetic flux density, excellent in soft magnetic characteristics, high in specific resistance, and excellent in writing performance, so that suitable for the magnetic substance of a thin film magnetic head. The plated thin film can be manufactured according to the manufacturing method of the invention. As a further additional effect, by the mixture of Mo, W, Cr and V in a plated thin film, the corrosion resistance is increased. Further, since plating is performed on the condition of low current density according to the method of the invention, the invention is excellent in controllability of film thickness, and further it is possible for the invention to control the magnetostriction constant by the utilization of the fact that by varying current density the film composition is changed.

[Brief Description of the Drawings]

Fig. 1 is a drawing showing the distribution of saturation magnetic flux densities in a Co-Ni-Fe ternary series alloy.

Fig. 2 is a drawing showing the plating bath of a paddle stirring type used in the example.

Fig. 3 is a drawing showing the relationship between the contents of addition elements and the concentration of added ions of the soft magnetic plated thin films manufactured according to the example of the invention.

Fig. 4 is a drawing showing the relationship between the contents of addition elements and the specific resistance and saturation magnetic flux density of the soft magnetic plated thin films manufactured according to the example of the invention.

[Description of Reference Numerals and Signs]

- 1: Plating layer
- 2: Cathode
- 3: Anode
- 4: Paddle